Studies on Chloroalkylethers of Various Alcohols

AUTHOR(S):

Oda, Ryohei; Teramura, Kazuhiro

CITATION:

Oda, Ryohei ...[et al]. Studies on Chloroalkylethers of Various Alcohols. 京都大学化学研究所報告 1951, 26: 88-89

ISSUE DATE:

1951-12-10

(IX), with mol. wt. 370–80, 450–65 and 590–600, respectively. Also hydroquinone, hydroquinone monomethyl ether and resorcinol gave resinous products, (X), (XI) and (XII). The mol. wts. could not be determined. 4,6-Dimethylol-o-cresol and p-cresol afforded amorphous solid (XIII), mol. wt. 380–90.

On standing for few days the mixt. of 1 mol of eugenol, equivalent amount of 20% NaOH 2 mol of HCHO as formalin gave yellow viscous oil (XIV), mol. wt. 470–500. Similarly thymol resulted brilliant yellow solid (XV), mol. wt. 550–70.

The activities of these new antioxidants were tested by comparing the oxygen absorption velocities of linseed oil which dissolved the various samples. Crystalline, high melting products, (V) and (VI), were inactive. (IX), (XI) and (XIV) had high activities as Ionol (2,6-di-tert.-butyl-p-cresol). (VII), (VIII) and (XIII) were somewhat weaker than Ionol. Cresol-analogs of NDGA were inactive.

---

27. Studies on Chloroalkylethers of Various Alcohols

Ryohei Oda and *Kazuhiro Teramura*

(Oda Laboratory)

I. Some new reactions.

The chlorine atom of choralkylethers of alcohols obtained by the action of formaldehyde and hydrochloric acid upon alcohols, is very reactive, but only a few examples are known till now about the reactions of these compounds.

The authors accordingly tried to elucidate the chemical reactions of these compounds and succeeded in the following reactions.

(1) $C_6H_5OK + ClCH_2OCH_3 \longrightarrow C_6H_5OCH_2OCH_3$ 83% (in ether)

(2) $C_6H_5NH_2 + ClCH_2OCH_3 \longrightarrow C_6H_5NHCH_2OCH_3$ 17% (in ether)

(3) $CH_3COCHCOOC_2H_5 + ClCH_2OCH_3 \rightarrow CH_3COCHCOOC_2H_5$ 30% (in alcohol)
(Na; CH_2OCH_3)

(4) $CH_3OCH_2Cl + ClCH_2OCH_3 \rightarrow CH_3OCH_2CH_2OCH_3$ 50% (Wurz-Fittig's reaction)

(5) $C_6H_6 + ClCH_2OCH_3 \rightarrow C_6H_5CH_2OCH_3$ 23% (Friede-Krafts reaction)

II. Condensation of chloroalkylethers by copper powder into dialkylglycolether

As is well known, the halogenalkyls condense into bi-alkyls by the aid of metalic sodium (Wurz-Fittig's reaction).

This reaction also occurs in the case of chloromethylethylethers of alcohols.

But the authors have discovered that this condensation can be achieved by metalic copper or iron instead of metalic sodium, and the corresponding dialkyl-ethers of glycols were obtained. The results are summerised in the following table.

(1) $2CH_3OCH_2Cl \longrightarrow CH_3OCH_2OH_2OCH_3$ 73% (70°c, 5hrs)

(2) $2C_2H_5OCH_2Cl \longrightarrow C_2H_5OCH_2CH_2OC_2H_5$ 70% (80°c, 5hrs)

(3) $2C_4H_9OCH_2Cl \longrightarrow C_4H_9OCH_2CH_2OC_4H_9$ 66.6% (150°c, 3hrs)

(4) $2C_4H_9OCHCH_3 \longrightarrow C_4H_9OCH{-}CHOC_4H_9$ 50.5% (120°c, 5hrs)
(Cl; CH_3 CH_3)

(5) $2C_4H_9OCHC_3H_7 \longrightarrow C_4H_9OCH{-}CHOC_4H_9$ 54% (110°c, 10hrs)
(Cl; C_3H_7 C_3H_7)

(6) $2C_4H_9CHCH_2OCH_2Cl \longrightarrow C_4H_9CHCH_2OCH_2CH_2OCH_2CHC_4H_9$ 41%
(C_2H_5; C_2H_5; C_2H_5) (150°c, 10hrs)

(7) $2ClCH_2CH_2OCH_2Cl \longrightarrow ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$ 50.5% (140°c, 10hrs)

(8) $2C_{12}H_{25}OCH_2Cl \longrightarrow C_{12}H_{25}OCH_2CH_2OC_{12}H_{25}$ 52% (130°c, 10hrs)

(9) $2C_{16}H_{33}OCH_2Cl \longrightarrow C_{16}H_{33}OCH_2CH_2OC_{16}H_{33}$ 50% (130°c, 3hrs)

---

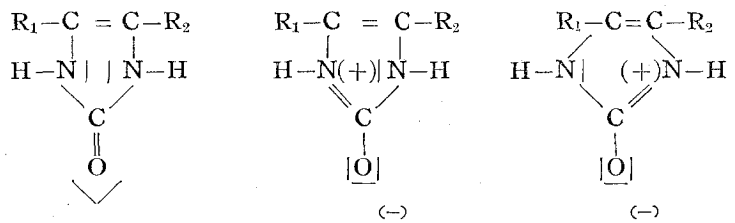
28. Studies on the Syntheses of Organic Fluorescent Compound. (I-II)

Ryohei Oda and *Zen-ichi Yoshida*

(Oda Laboratory)

I. Synthesis of Imidazolone Derivatives from Acyloins and Urea.

Imidazolone ring, which has a ethylene bond and a ureido group, resonates as follows:



It is considered accordingly, that ureido group is a kind of -M substituent, and imidazolone ring has a favourable constitution on the emissivity of fluorescence from the present authors' theory concerning the fluorescence and chemical constitution of organic compounds.

As a matter of fact, 4,5-diphenylimidazolone, in which two phenyl groups are conbined respectively with 4th and 5th positions of imidayolone ring, and the conjugation system is thus being enlarged, strongly fluoresces blue-violet rays in both solid and solution states under ultra-violet rays.

We synthesized several imidazolone derivatives and thioimidazolones.

As to the synthetic method we refered to Org. Synth. Collect. Vol. II. p. 222.